State of the Art in GaP Electroluminescent Junctions*

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Quantum efficiencies and brightness values for green and particularly for red light emission from currently available GaP p-n junctions in forward bias at room temperature are sufficiently high to merit consideration in electroluminescence applications where the human eye is the detector.

I. INTRODUCTION

Although the recombination radiation from forward-biased GaP p-n junctions could be used for the same applications as the emission from lower band-gap materials (e.g., in photon-coupled circuitry), the GaP emission occurs mainly in the visible portion of the spectrum and is thus more appropriate for applications where the human eye is the detector. To obtain emission in the visible from a forward-biased p-n junction, one needs a semiconductor with a band gap greater than 1.8 eV. The II–VI compounds that meet this requirement cannot be made into simple p-n junctions (although some of their alloys can). Hence, only GaP, BP and the various polytypes of SiC are considered. (These are all indirect gap semiconductors so that stimulated emission is not normally expected.) Of these three, GaP (band gap 2.26 eV) is characterized by the simplest materials technology.

II. RADIATIVE RECOMBINATION MECHANISMS

Fig. 1 shows a typical room temperature forward-bias emission spectrum from a diode prepared by Zn diffusion into an n-type crystal containing Te and O. Two emission bands appear in the visible, separated both spectrally and spatially. A weak green band is generated

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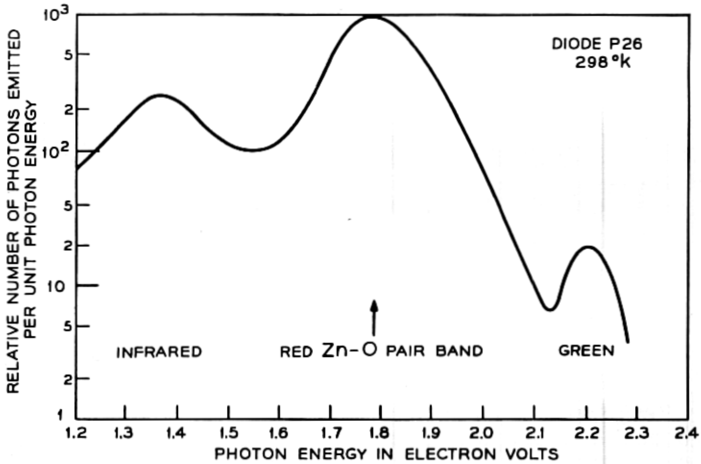

Fig. 1 — Emission spectrum from a forward biased Zn-diffused diode at room temperature.

close to the junction proper, while a much stronger red band seems to originate on the p-side of the junction. Infrared emission seen in Fig. 1 will not be discussed.

2.1 *The Red Emission*

Mostly by comparison with photo-luminescence, it has been shown that the red band is due to donor-acceptor pair recombination involving shallow Zn acceptors and deep O donors.[1] External photoluminescence quantum efficiencies of up to 11 percent have been reported at room temperature in p-type samples.[2] Zn-O pair band recombination in a p-n junction is sketched in Fig. 2. On the p-side of the junction the Zn level ($N_A \approx 2 \times 10^{18}$ cm^{-3}) is about half full of holes in thermal equilibrium. Injected minority carrier electrons are captured efficiently by the ionized compensating O donors and, because the O donor is relatively deep, the electrons remain trapped, with little thermal ionization back to the conduction band, until they recombine radiatively with holes on the Zn acceptors. This situation is identical to the Zn-O pair emission in photoluminescence and should lead to high efficiencies. On the n-side of the junction, the O donors are always filled with electrons. Injected minority carrier holes may be captured by the empty Zn acceptors, but, because the Zn acceptor level is quite shallow, they are thermally released back to the valence band, from where they may find other means to recombine. In the space-charge

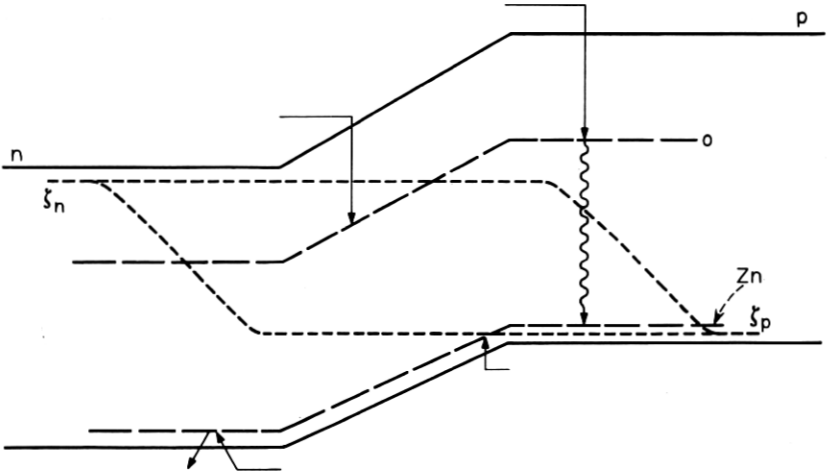

Fig. 2 — The Zn-O pair band mechanism in a forward-biased p-n junction.

layer, the O donors are below the electron quasi-Fermi level from the n-side to deep into the depletion layer, and these donor states can be populated by electrons. However, the Zn acceptors lie above the hole quasi-Fermi level only very close to the p-side. It is only these acceptors that contain trapped holes. Hence, there is no region in the space-charge layer that contains both trapped electrons and trapped holes, and therefore, the Zn-O pair band should not be an efficient recombination mechanism in the depletion layer. Thus, we expect the red Zn-O band to originate predominantly from the p-side, beyond the space-charge layer.

2.2 *The Green Emission*

Among the many types of recombination leading to photoluminescence near the band edge at low temperatures there are (*i*) pair transitions involving a shallow donor and a shallow acceptor (e.g., Te and Zn),[3, 4] and (*ii*) the "A" line and its phonon replicas due to exciton recombination at an N atom substituting isoelectronically for a P atom.[5,6] The green emission at low temperatures observed from junctions prepared from such material can be identified as due to these transitions by simply comparing electroluminescence and photoluminescence spectra.[7] As the temperature of the diodes is increased, the pair band becomes weaker and the "A" line grows at first but then also diminishes in intensity and, at the same time, it broadens and merges with its phonon replicas. Above approximately 200°K, only a broad green emission band remains. It is, therefore, not clear whether the room temperature green band is due to isoelectronic N traps, or to shallow pairs, or to some new mechanism. The possibility of simple band-to-band recombination can be eliminated because the observed efficiency is several orders of magnitude greater than the efficiency (on the n-side, on the p-side, and in the space-charge layer) calculated using the band-to-band rate constant derived from a detailed-balance analysis of the absorption edge.

III. INJECTION — RECOMBINATION KINETICS

3.1 *Dominant Current*

The current-voltage characteristics of Zn-diffused diodes can be explained quantitatively by assuming that there are several current generating mechanisms, each of which dominates in a different range of forward bias.[1] These mechanisms are summarized in Table I. We assume that the current J can always be written as exp qV/nkT, where n will depend upon bias. At the lowest applied bias, surface leakage predominates and the effective n (at room temperature) is about four. In the next bias range the dominant current is due to recombination at deep levels in the space-charge layer. Here $n = 2$, but with increasing bias, preexponential terms (W is the junction width and V_D the built-in potential) cause the effective value of n to decrease. In the next bias range, not observed in all diodes, recombination at a shallow level in the space-charge layer dominates. Although n is nominally equal to unity here, again pre-exponential terms perturb its value somewhat. Here the effective n lies between one and two and slowly decreases toward unity with increasing bias. Thus, in the space-charge regime, n starts at two, and approaches one at high bias. Finally, at the highest biases, simple injection beyond the depletion layer dominates with $n = 1$. (Conductivity modulation which should set in at even higher biases has so far not been observed.)

3.2 *Red Emission*

We have already noted that the red Zn-O emission seems to originate from the p-side of the junction. From near-field spatial distributions on a surface cleaved perpendicular to the junction plane it is evident that the green emission, at least at high biases, is centered at the junction itself, as defined by observations of the junction electro-

Table I — Dependence of Current (J) and of Zn-O Pair Band Emission (L) upon Bias (V) and Their Comparisons

Dominant Current, J

$$J \propto \exp \frac{qV}{nkT}$$

Surface Leakage	Space Charge Recombination		Diffusion Current on n-Side	
	Deep Levels	Shallow Levels	Linear Range	Conductivity Modulation
$J \alpha \exp \beta V$	$J \alpha \frac{W}{V_D - V} \exp \frac{qV}{2kT}$		$J \alpha \exp \frac{qV}{kT}$	
$\beta \approx q/4kT$ $n \approx 4$	$n \leqq 2$	$n \rightarrow 1$	$n = 1$	$n = 2$

$L \alpha J^4$	$L \alpha J^2$	$L \alpha J^1$	$L \alpha J^{1/2}$

$m = 1$ $L \alpha \exp \frac{qV}{kT}$	$m = 2$ $L \alpha \exp \frac{qV}{2kT}$	$m = \frac{n}{n+1}$	$m = 2$
Linear Range	Diffusion	Diffusion and Drift	Conductivity Modulation
	Saturation		

Light Emission from p-Side, L

$$L \alpha \exp \frac{qV}{mkT}$$

optic effect.[1] However, the red emission is not centered on the junction but lies on the p-side. At high biases the emission closest to the junction saturates and the emission volume simultaneously expands deeper into the p-side. This observation is inconsistent with n-side or space-charge layer recombination.[1] Thus, the red emission is generated on the p-side beyond the space-charge layer, as expected from Fig. 2. The spatial motion at high biases is due to the saturation of the recombination centers on the p-side.[8] The injected carriers, therefore, must travel beyond the normal diffusion length in order to recombine. We again assume that we can write the red light intensity L in the form exp qV/mkT. At low bias, with simple injection into the p-side and recombination at Zn-O pairs, $m = 1$. However, in the saturation range at high bias, with minority carrier transport limited by diffusion only, $m = 2$.[8]

3.3 *Green Emission*

It is an experimental result that m is always equal to unity for the green emission, independent of the bias.

3.4 *Light versus Current*

In Table I the J-V and L-V data (for the red band) are combined to show the dependence of light intensity upon current. At low bias, where surface leakage predominates, the light emission varies as $\approx J^4$. In the space-charge regime the relationship is quadratic, but it approaches linearity at high bias. At the highest biases, with saturation on the p-side, and with the current due to injection beyond the space-charge layer (hence, into the n-side), the relationship becomes sublinear. Thus, the quantum efficiency of the Zn-O red band increases rapidly at first, then slowly levels off and finally decreases at the highest biases, thus exhibiting a maximum in the linear range. For the green emission $m = 1$ always. Hence, the quantum efficiency rises rapidly, then slowly levels off and remains constant up to the highest biases measured.

IV. DIODE STRUCTURES

The various types of GaP p-n junctions that have been reported in the literature are summarized in Table II. The circled structures were prepared expressly to exhibit the Zn-O red band. A typical in-diffused diode is made by diffusing Zn into an n-type crystal containing Te and O. A typical out-diffused diode is made by heating a p-type crystal doped with Zn, Te, and O, so that some Zn diffuses out, leaving an n-layer near the surface. Grown junctions may be prepared by floating-zone,[9,10] by vapor phase epitaxy[10,11] or by solution-growth epitaxy.[12,13] For example, in the latter case one can grow (by "tipping") an n-type Te-doped layer from solution onto a p-type seed containing Zn + O.[12] A typical alloyed diode is made by alloying a Sn ball onto a p-type sample containing Zn + O.[14,15,16] Finally, surface structures may be prepared by evaporating a metal on a cold p-type substrate containing Zn, Te, and O.[16]

The diffused structures and the grown junctions are simple p-n

TABLE II — GaP DIODES (CIRCLED) DESIGNED TO EXHIBIT THE Zn-O RED PAIR EMISSION

GaP Junctions								
Diffused			Grown		Alloyed		Surface	
In-Diffused		Out-Diffused						
Substrate	Diffusant	Substrate	Method	Doping	Substrate	Alloy	Substrate	Film
n	Zn	p	Float-zone	Mg-S	p	Sn	p	Au
(Te + O)	Cd	(Zn + Te + O)		Cd-S	(Zn + O)	Ag-Te	(Zn + Te + O)	Sn
		(Cd + Te + O)	Vapor	Mg-S	n	In-Zn		Ag paste
p	Si			Cd-S		Au-Zn		
			Solution	(Zn + O)-Te		Ag-Zn		
p-n		p-n	p-n		p-n Surface-barrier, tunneling		Tunneling	

junctions, where injection is due to thermal activation over the normal junction barrier.[1] In the surface diodes injection arises from tunneling through a thin surface layer.[16] Three injection mechanisms can occur in parallel in the alloyed diodes.[16] In the regions where Sn alloying produces an n-type regrowth layer on the p-type substrate, a simple p-n junction is formed. In regions where no n-type regrowth layer is produced, the metal is in intimate contact with the p-type substrate. This is a surface barrier junction which at forward bias can only extract majority carrier holes. Since it cannot inject minority carriers it results in an excess nonradiative current component. In regions where a thin layer of insulator (perhaps an oxide) separates the metal from the substrate, it is also possible to inject minority carriers by tunneling.

V. RADIATIVE EFFICIENCIES

5.1 *Quantum Efficiency*

Table III summarizes the maximum reported external quantum efficiencies of the red Zn-O band at room temperature in the five classes of diodes described previously. Note that while the highest measured efficiency, 1.5 percent, corresponds to an alloyed diode,[17] the maximum efficiencies observed in the other four classes are all within less than a factor of ten of this value. The table also lists some "average" efficiencies,[12,14] which is the range obtainable with high yields with present technology. The highest quantum efficiency reported for the green emission is 0.015 percent,[18] or 100 times less than the corresponding figure for the red. Since the external quantum efficiencies for spontaneous emission in GaAs diodes at room temperature are usually one to five percent, it is obvious that the red emission from GaP, only slightly less efficient, might be useful in applications where spontane-

TABLE III — EXTERNAL QUANTUM EFFICIENCIES OF Zn-O PAIR BAND IN GaP DIODES AT ROOM TEMPERATURE

		Maximum (%)	Average (%)	Source
In-diffused	Zn/Te + O	0.2		BTL
Out-diffused	Zn + Te + O	0.7		BTL
Solution-grown	Te/Zn + O	0.75	0.3–0.5	IBM
Alloyed	Sn/Zn + O	1.5		Philips
			0.01–0.1	SERL
Surface	Au/Zn + Te + O	0.4		BTL

ous GaAs emitters are considered, as in optoelectronic devices. However, the significant distinction is that the GaP emission lies in the visible range.

5.2 *Luminous Efficiency*

By integrating the product of the emission spectrum of the Zn-O red band and the visual acuity curve, it is found that one watt of Zn-O red light is equivalent to 20 Lumens as far as the eye is concerned. The GaP green emission corresponds to about 650 Lumens/watt. (For comparison, the emission from GaP_xAs_{1-x}, where x corresponds to the maximum P concentration before the band structure becomes indirect, is equivalent to approximately 100 Lumens/watt.) Consider a typical diode, available with current technology, as summarized in Table IV. It may operate at 20 mA with a dc bias of 2 volts emitting red light with an external quantum efficiency of 0.5 percent. (Since the energy of the emitted photon is 1.77 eV, the power efficiency is only slightly less than the quantum efficiency.) With a junction area of 10^{-3} cm^2 the current density is 20 amps/cm^2, which is close to the maximum in quantum efficiency. Table IV also notes the output in normal power units as well as in luminous units. By assuming that the light leaves the diode from only one surface in the active junction area of 10^{-3} cm^2, the predicted brightness is 3600 foot-Lamberts. (Although present measurements are about a factor of ten lower, the discrepancy might be decreased by using large ratios of active junction area to inactive surfaces, or by using special geometries or index-of-refraction-matching glasses to increase the light output from a given region.) The maximum reported efficiency for the green emission is only 0.015 percent but the luminous equivalent of the

TABLE IV — TYPICAL LUMINOUS EFFICIENCY FOR THE Zn-O RED BAND (20 LUMENS/WATT)

Typical diode:	20 mA
	2 V
	0.5% external quantum efficiency
	10^{-3} cm^2 area
Output:	2×10^{-4} watts
	4×10^{-3} Lumens
	3×10^{-4} candles
Brightness:	4 lamberts
	3600 foot-Lamberts
	1200 candles/square foot

green band is more than 30 times greater than that for the red band. Thus, the brightness currently available from the *best* green diodes are approximately equal to that available from current *average* red diodes at biases where the red efficiency is a maximum. (At higher biases the green emission of course will increase more rapidly than the red emission.) For comparison, the brightness of the green emission from a ZnS:Cu electroluminescent cell is about 1 foot-Lambert (at 60 Hz, and up to 10 foot-Lamberts at higher excitation frequencies, but with significant deterioration during aging). Thus, with present technology, the red emission from GaP diodes corresponds to much higher brightness values than for standard ZnS EL cells, and this occurs in the bias range corresponding to maximum efficiencies — 0.3 to 0.5 percent quantum efficiency. Similarly, the brightness of the GaP green emission is also higher than that available from ZnS panels.

5.3 *Efficiency Outlook*

Since the quantum efficiency of the Zn-O red band is as high as 11 percent in photoluminescence of p-type samples, it might be possible to obtain similar electroluminescence efficiencies from p-side injection in junctions. At low to moderate biases the dominant competing mechanism is due to space-charge recombination at deep levels. Thus, a reduction of this current component could increase the red emission efficiency. Since the room temperature green emission mechanism has not been established, similar predictions for the green band cannot be made. Finally, it is noted that a number of other deep pair combinations exhibit donor-acceptor pair recombination in the orange and red in photoluminescence at room temperature with efficiencies of several percent.[19,20] These may eventually provide useful recombination centers in GaP diodes.

VI. SUMMARY

Currently available p-n junctions in GaP emit in the red with an external quantum efficiency (roughly equal to a power efficiency) which exhibits a maximum (with bias) of 0.1 to 0.5 percent. The brightness at this maximum is within a factor of 10 of 3600 foot-Lamberts, far greater than that from a normal ZnS EL cell. The *best* green emitting diodes available correspond to a similar brightness value, but the efficiency does not drop with increasing bias. Such diodes should possess the normal advantages of semiconductor devices: low dc operating bias, small size, probably cheap to manufacture and hopefully little deterioration with aging. Special diode geometries or the use of index-of-refraction-matching glasses might be used to increase the external quantum efficiency (although the red band falls in a region of low internal absorption, the green band, near the band edge, does not) or to focus the emitted light, thereby increasing the apparent brightness.

REFERENCES

1. Gershenzon, M., Logan, R. A., and Nelson, D. F., Phys. Rev., *149,* 1966, p. 580.
2. Gershenzon, M. and Mikulyak, R. M., Appl. Phys. Letters, *8,* 1966, p. 245.
3. Thomas, D. G., Gershenzon, M., and Trumbore, F. A., Phys. Rev., *133,* 1964, p. A269.
4. Trumbore, F. A. and Thomas, D. G., Phys. Rev., *137,* 1965, p. A1030.
5. Thomas, D. G., Gershenzon, M., and Hopfield, J. J., Phys. Rev., *131,* 1963, p. 2397.
6. Thomas, D. G., Hopfield, J. J., and Frosch, C. J., Phys. Rev. Letters, *15,* 1965, p. 857.
7. Gershenzon, M., Mikulyak, R. M., Logan, R. A., and Foy, P. W., Sol. St. Elect., *7,* 1964, p. 113.
8. Nelson, D. F., Phys. Rev., *149,* 1966, p. 574.
9. Frosch, C. J. and Derick, L., J. Electrochem. Soc., *108,* 1961, p. 251.
10. Gershenzon, M. and Mikulyak, R. M., Sol. St. Elect., *5,* 1962, p. 313.
11. Frosch, C. J., J. Electrochem. Soc., *111,* 1964, p. 180.
12. Lorenz, M. R. and Pilkuhn, M., J. Appl. Phys., in press.
13. Trumbore, F. A. and Logan, R. A., to be published.
14. Allen, J. W., Moncaster, M. E., and Starkiewicz, J., Sol. St. Elect., *6,* 1963, p. 95.
15. Grimmeiss, H. G. and Koelmans, H., Phil. Res. Rpts., *15,* 1960, p. 290; Phys. Rev., *123,* 1961, p. 1939; Grimmeiss, H. G., Rabenau, A., and Koelmans, H., J. Appl. Phys., *32,* 1961, p. 2123.
16. Logan, R. A., Gershenzon, M., Trumbore, F. A., and White, H. G., Appl. Phys. Letters, *6,* 1965, p. 113.
17. Grimmeiss, H. G. and Scholz, H., Phys. Letters, *8,* 1964, p. 233.
18. Pilkuhn, M. H. and Foster, L. M., IBM J., *10,* 1966, p. 122.
19. Gershenzon, M., Trumbore, F. A., Mikulyak, R. M., and Kowalchik, M., J. Appl. Phys., *37,* 1966, p. 486.
20. Gershenzon, M., Trumbore, F. A., Mikulyak, R. M., and Kowalchik, M., to be published.